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(54) Title: BLEACHING OF LIGNIN AND PROCESS FOR PRODUCING PAPER

(57) Abstract: The present invention relates to the bleaching of lignin present in pulp fibers in an aqueous environment such as a pulp suspension. The invention also relates to a process for producing paper or board from pulp containing such bleached lignin. According to the invention carbon dioxide is used for the bleaching of lignin.

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## **Bleaching of lignin and process for producing paper**

The present invention relates to the bleaching of lignin present in pulp fibers in an aqueous environment such as a pulp suspension. The invention also relates to a process for producing paper or board from pulp containing such bleached lignin.

Lignin is an amorphous polymer which, like a glue, keeps the cellulose fibers together in wood. Some lignin also exist in the fiber wall. In its native state in wood lignin is of light color.

The purpose of chemical pulping, such as kraft pulping, is to dissolve the lignin from the wood matrix with a cooking liquor. During cooking lignin is broken down into smaller units and becomes darker, i.e. increases the light absorption. The dark lignin components, some of which are dissolved and some of which are still in the fiber, give the pulp a dark colour.

In the production of paper or board a large proportion of the lignin is washed off the fibers in one or more washing steps. According to EP 296198 (AGA Aktiebolag) the washing-out of substances which contribute to the chemical oxygen demand (COD) in an alkaline cellulosic pulp is improved if the pH of the wash water is lowered with an acid such as carbon dioxide. According to an article by Östberg, G., 5th International Conference of New Available Technique, The World Pulp and Paper Week, June 4-7, 1996, Stockholm pp. 508-515, the said improved washing results in an increased degree of delignification and a consequent decrease in the consumption of bleaching chemicals. Calcium carbonate is formed in a reaction between calcium and the carbonate ions generated by the carbon dioxide. No increase of calcium carbonate deposition on the equipment was observed.

Sundin, J. et al. in "Precipitation of lignin during pulp washing", p. 219-227, proceedings, TAPPI Pulping Conference, 1998, discloses that the addition of calcium or magnesium ions to deionized water used for washing a pulp provided washed pulps with a higher kappa number (a common measure of the lignin content) than pulps washed without addition of these ions. There was found to be a correlation between kappa number and the concentration of calcium, magnesium and the like ions in the wash water. The more ions were added, the higher the kappa number.

Sundin et al. also showed that lignin which precipitated during washing with water to which calcium ions had been added was darker than the other residual lignin in the pulp. Pulps washed with water containing calcium ions were significantly darker than those without such ions.

In a recent publication Gustavsson, C. et al. Nordic Pulp and Paper Research Journal Vol 14, No 1, 1999, p 71-81, noted a distinct decrease in the content of calcium when cooking with a high hydroxide ion concentration. An explanation to the phenomenon is said to be that the calcium is bound to dissolved lignin fragments at high hydroxide ion concentration and, consequently, there is a decreased precipitation of calcium carbonate on the pulp fibers.

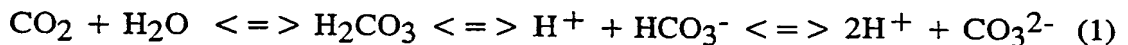
On the other hand, WO 90/09483 (Mo och Domsjö Aktiebolag) utilizes the tendency of calcium carbonate to precipitate at an alkaline pH for reducing the amount of gypsum (calcium sulphate) precipitation in a paper stock. A precipitation of the calcium carbonate is induced by adding (bi)carbonate ions to the system. The ions may be created *in situ* by an addition of sodium hydroxide and carbon dioxide.

According to WO 99/00545 (Sunds Defibrator Industries AB) the release of calcium ions into the filtrate of a papermaking system by acidic bleaching conditions below pH 7 cause harmful precipitations on the equipment. The calcium ions are absorbed on the pulp by an addition of carbonate ions and removed with the pulp

According to US 5,139,613 (Canadian Liquid Air Limited) carbon dioxide is used to acidify a pulp slurry after it has been bleached with hypochlorite or hydrogen peroxide. The souring with CO<sub>2</sub> instead of SO<sub>2</sub> does not destroy the bleaching chemical which allows the residual bleaching chemicals to continue their bleaching effect for a longer time.

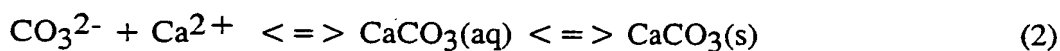
According to GB Patent Application 2 008 562 carbon dioxide may be used for increasing the solubility of calcium carbonate and for the hardening of recycled waters used in the treatment of pulp from waste paper.

Carbon dioxide is a gas, which easily dissolves under alkaline conditions, e.g. in water or a pulp suspension forming carbonic acid and bicarbonate and/or carbonate ions according to the reaction:



Water soluble salts of carbonic acid such as sodium bicarbonate  $\text{NaHCO}_3$  and sodium carbonate  $\text{Na}_2\text{CO}_3$  also provide bicarbonate and carbonate ions in an aqueous environment.

Carbonate ions have the ability of being bound to calcium ions and of creating calcium carbonate, which is a salt with a low solubility at alkaline pH:



At a pH below about 8 calcium carbonate starts to dissolve and the concentration of free calcium ions increases. High concentrations of free calcium ions in a papermaking system are known to cause complex coagulation and scaling problems in papermaking.

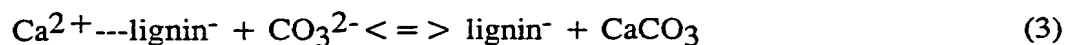
The present invention, as defined in the appended claims, is based on the realization that carbonic acid and salts thereof, which provide carbonate and bicarbonate ions, can be used for bleaching calcium containing lignin dissolved or present in pulp fibers in an aqueous pulp suspension.

Although not wishing to be bound by any theory, it is believed that the (bi)carbonate ions are capable of trapping calcium present in the system and thus reducing the influence of calcium on the lignin. This, in turn, provides lignin compounds in the pulp which are lighter in colour. The bleached lignin compounds may also be easier to remove from the fibers causing the pulp to have a reduced lignin content. In either case, the paper resulting from the (bi)carbonate bleached pulp will have an increased brightness. Thus, such a pulp requires a reduced amount of other bleaching chemicals to provide the desired brightness.

The carbonic acid is preferably provided by dissolving carbon dioxide gas in the aqueous pulp suspension. The dissolved gas will produce carbonic acid in the water and will, in turn, provide carbonate and/or bicarbonate ions in the suspension. Carbon dioxide may also be added in liquid or solid form to the suspension.

The carbonates/bicarbonates in the aqueous environment will associate with calcium ions in said environment in such a way that the calcium ions become "trapped" in calcium carbonate. This will reduce the amount of calcium available to influence the lignin. The

result will show up as an increased brightness and possibly also as a lower kappa number in the pulp:



For a high kappa pulp intended to be used in its unbleached form, for example in packaging grades such as linerboard and sack paper, the result of carbon dioxide addition and consequent calcium ion removal from lignin is a brighter pulp/paper with very likely also a lower kappa number at the same cooking conditions. This pulp/paper can be used as such as an unbleached product with higher brightness or the product may provide savings in the top layer of bleached fiber and coating added for optical/printing purposes. The lignin bleaching effect can also be utilized for producing a pulp with the same kappa number as before but with less severe cooking conditions, which means increased productivity, steam savings, increased selectivity or savings in cooking chemicals.

For a pulp intended to be bleached, reducing the influence of calcium ions on lignin makes a pulp with a improved bleachability; consuming less bleaching chemicals to a given brightness.

To reach the desired effect, the carbon dioxide may be added at various positions in the fiber line or the papermachine. It should be observed that the (bi)carbonate ions required in the bleaching process may also be provided by adding carbonic acid or salts of carbonic acid, i.e. (bi)carbonate salts such as sodium bicarbonate or carbonate to the pulp suspension.

The preferred way of providing the carbonate/bicarbonate ions is to add carbon dioxide gas to the aqueous pulp suspension. From a dissolving point of view of the carbon dioxide should preferably be added to an aqueous medium in an alkaline state. Thus, a pH around 8 or above is preferred. On the other hand, the value of inactivating deleterious calcium ions in lignin is highest at a lower pH when less phenolic groups are ionized and the lignin molecules have a higher tendency to precipitate. The pH decreasing effect of the addition of carbon dioxide may be countered by the addition of an alkali such as sodium hydroxide to the solution.

The optimum pH at which to add CO<sub>2</sub> depends on the number of groups in the lignin with the capacity to become ionized (normally a function of kappa number, cooking method, wood type), the purity of the cooking chemicals and water purity. As the lignin which is most difficult to remove is left in the pulp to the last bleaching stage and its number of ionized groups is low, CO<sub>2</sub> addition before such stage to trap any calcium ions present, can be especially beneficial.

One should avoid adding CO<sub>2</sub> when a high amount of the black liquor is present. A publication by Hartler ("Sorption cooking", Svensk Papperstidning, p 457-463, No 14, 1978) describes sorption cooking, a method where CO<sub>2</sub> addition increases yield by re-deposition of lignin from the black liquor to the fiber. Using the same chemical (CO<sub>2</sub>) sorption cooking has quite the opposite effect to the process described in this patent application.

In the case of a high kappa pulp one suitable location to add CO<sub>2</sub> is to the outlet of final storage in the pulp mill from where the pulp is transported to storage in the paper mill. CO<sub>2</sub> can either be added to the dilution water or directly to the pulp.

The pulp is preferably a chemical pulp. The pulp may or may not be delignified in an oxygen delignification stage. One preferred stage of adding CO<sub>2</sub> is before a D-stage bleaching, preferably before a storage tower before such bleaching. The CO<sub>2</sub> may also be added to a pulp which is subsequently to be bleached with chlorine dioxide, peroxide, peracetic acid, ozone, chlorine, hypo, or the like bleaching chemical. Another preferred position is before, after or in a wash stage in the fiber line of a pulp mill. Adding bleaching CO<sub>2</sub> after a wash stage wherein a large proportion of the lignin has been removed by washing is especially effective.

In a preferred embodiment of the invention the pulp is a chemical pulp which has been washed and carbon dioxide is fed into a stream of pulp between a wash stage and a storage at the end of the fiber line of a pulp mill. The carbon dioxide is preferably fed into a stream of water used to dilute the pulp prior to final storage in the fiber line.

The calcium trapped by said carbon dioxide from said lignin may be removed from said pulp suspension by a press stage or a wash stage preceding storage or the like process.

The pulp to be treated according to the present invention may also be a papermaking stock before, after or in a stock preparation stage of a paper mill. Examples of such stock preparation stages are a dilution stage, a refining stage, a screening stage and a mixing stage.

The carbon dioxide may be introduced into a stream of white water in the long or the short circulation of a papermachine.

The present invention is preferably utilized in the production of paper or board whereby paper or board is produced having an increased brightness and/or a reduced kappa number, compared to paper or board produced without the (bi)carbonate addition, by a process comprising

- providing a chemical pulp suspension of cellulosic fibers and calcium containing lignin compounds in an aqueous environment,
- providing carbonic acid or a salt thereof in said suspension or in a stream of water entering said suspension for causing a substantial bleaching of lignin present in said suspension and/or for facilitating the freeing of calcium containing lignin from the fibers in said suspension,
- processing said suspension into paper or board.

The lignin which is bleached by the present process is generally a calcium-containing lignin and the amount of carbon dioxide or carbonic acid salt added to the suspension should be sufficient to trap a significant amount of the calcium present in the suspension, thus providing a lighter coloured lignin which will also more easily be freed from the fibers.

The following examples illustrate the invention:

#### Example 1

CO<sub>2</sub> was added to a high kappa pulp at the outlet from the final storage in a pulp mill from where the pulp was transported to storage in the paper mill. The CO<sub>2</sub> was added to the dilution water and the brightness of the final product, the paper, became 2 ISO units brighter.

**Example 2**

In a case of a softwood kraft pulp to be bleached with chlorine dioxide, 3 kg CO<sub>2</sub>/ton of pulp was added before 30 minutes storage after which the pulp was pumped to the chlorine dioxide bleaching stage. 3 kg CO<sub>2</sub>/ton of pulp addition resulted in 3 kg ClO<sub>2</sub>/ton of pulp savings in the bleach plant to reach the same bleach result.

**Example 3**

In a case of kraft pulp to be bleached in a TCF sequence with peroxide 4 kg CO<sub>2</sub>/ton of pulp was charged to the dilution water of the pulp before the final wash stage before bleaching. In the bleach plant the bleach chemical consumption was reduced with 5 kg H<sub>2</sub>O<sub>2</sub>/ton pulp.

**Example 4**

A laboratory test was performed in a Quantum mixer. A softwood kraft pulp with kappa number 65 was used. The pulp was diluted with de-ionized water to a consistency of 8 %. CO<sub>2</sub> gas was added to the pulp in the mixer under slow stirring. The pH was observed during 60 minutes treatment.

Thereafter the pulp was diluted with de-ionized water to a consistency of 1 %. The pulp suspension was divided in two samples, where one was adjusted to pH 5 with H<sub>2</sub>SO<sub>4</sub>. Sheets were prepared and the brightness was measured with an Elrepho instrument. The results of the trials is shown in the Table below.

**Table**

Trial No.	CO <sub>2</sub> kg/t	pH after 60 min.	Adjusted pH	Brightness % ISO	Unadjusted pH	Brightness %
4	0	8.2	5	19.8		
3	0	8.2			9.2	18.4
6	3	6.8	5	20.2		
5	3	6.8			8.5	19.3
8	9	6	5	20		
7	9	6			7.6	19.4
1	15	6.2	5	21.6		
2	15	6.2			7.1	20.8

The tests clearly show an increased brightness in response to an increased addition of carbon dioxide.



## Claims

1. Use of carbonic acid or a salt thereof for the bleaching of calcium containing lignin present in pulp fibers in an aqueous environment such as a pulp suspension.
2. The use according to claim 1 wherein said carbonic acid is provided by dissolving gaseous carbon dioxide in said aqueous environment, said carbonic acid dissociating in said aqueous environment and providing carbonate and/or bicarbonate ions.
3. The use according to claim 1 or 2 wherein the pH lowering effect of the carbonic acid is countered by the addition of an alkali such as sodium hydroxide to the aqueous environment.
4. The use according to claim 1 wherein a salt of carbonic acid such as sodium bicarbonate or sodium carbonate is dissolved into said aqueous environment for provided carbonate and/or bicarbonate ions.
5. The use according to any one of the preceding claims 1 to 4 wherein said aqueous environment is an aqueous pulp suspension or a filtrate from a dewatering stage.
6. The use according to claim 5 wherein said aqueous environment is a chemical pulp.
7. The use according to claim 6 wherein said chemical pulp is an unbleached or a semi-bleached pulp.
8. The use according to claim 6 wherein said chemical pulp is an unbleached pulp before, after or in a wash stage of a fiber line of a pulp mill.
9. The use according to claim 8 wherein said chemical pulp is an unbleached pulp just after a wash stage of a fiber line of a pulp mill.
10. The use according to claim 6 wherein said chemical pulp is a washed chemical pulp and carbon dioxide is fed into a stream of pulp between a wash stage and a storage at the end of the fiber line of a cellulose mill.
11. The use according to claim 6 wherein carbon dioxide is fed into a stream of water used to dilute the pulp just before or just after final storage of the fiber line.

12. The use according to claim 1 wherein calcium is trapped by carbonate or bicarbonate ions provided by said carbonic acid or its salt thereby reducing the influence of calcium on said lignin and facilitating the bleaching of lignin and/or freeing of lignin from fibers in said pulp suspension.
13. The use according to claim 6 wherein said chemical pulp is a pulp which has been bleached in an oxygen delignification step.
14. The use according to claim 6 wherein said chemical pulp is a pulp which is subsequently to be bleached with chlorine dioxide, peroxide, peracetic acid, ozone, chlorine, hypo, or the like bleaching chemical.
15. The use according to claim 14 wherein carbon dioxide is fed into a pulp added before, in or after a storage tower or to a dilution water added to said pulp before, in or after a storage tower preceding a chlorine dioxide bleaching stage in a fiber line of a cellulose mill.
16. The use according to claim 1 wherein said pulp is a papermaking stock before, after or in a stock preparation stage of a paper machine.
17. The use according to claim 16 wherein said stock preparation stage is a dilution stage, a refining stage, a screening stage or a mixing stage.
18. The use according to claim 16 wherein said carbon dioxide is introduced into a stream of white water in the long or the short circulation of a papermachine.
19. A process for producing paper or board comprising
- providing a chemical pulp suspension of cellulosic fibers and calcium containing lignin compounds in an aqueous environment,
  - providing carbonic acid or a salt thereof in said suspension or in a stream of water entering said suspension for causing a substantial bleaching of said calcium containing lignin present in said suspension and/or for facilitating the freeing of lignin from the fibers in said suspension,
  - processing said suspension into paper or board having an increased brightness and/or a reduced kappa number compared to a similar product produced without said carbonic acid or its salt.

20. The process according to claim 19, wherein said carbonic acid is provided by the introduction of carbon dioxide gas into said suspension or stream.

21. The process according to claim 19 or 20, wherein carbonic acid and/or an alkaline metal salt thereof is introduced in said suspension or in a stream of water entering said suspension in an amount sufficient for providing a chemically effective amount of carbonate and/or bicarbonate ions in said suspension for trapping a substantial amount of the calcium and reducing the amount of calcium influencing the lignin.

# INTERNATIONAL SEARCH REPORT

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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 D21C9/10 D21H23/04 //D21H21:32,D21H17:65		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 D21C D21H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
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<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center; font-weight: bold;">14 July 2000</div>		Date of mailing of the international search report  <div style="text-align: center; font-weight: bold;">20/07/2000</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center; font-weight: bold;">Naeslund, P</div>

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